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by Edgar L. Wong and Andrew E. Potter, Jr.

Lewis Research Center

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SUMMARY

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A mass-spectrometric stirred-reactor technique was used to study the reaction of atomic oxygen with methane with low concentrations of molecular oxygen. Low concentrations of molecular oxygen were used to suppress the reactions $O + O_2 + M \rightarrow O_3 + M$ and $H + O_2 + M \rightarrow HO_2 + M$.

An overall rate constant for oxygen-atom disappearance due to added methane was obtained for the temperature range of 375° to 576° K. This rate constant was $4.2 \times 10^{14} \exp(-10\,300/RT)$ and was compared with the previous rate constant for this reaction in the presence of a large excess of molecular oxygen. This comparison showed that the presence of an excess of molecular oxygen increased the oxygen-atom consumption only for the lower temperatures.

Product analyses indicated that the stoichiometry of the reaction could be represented by

$$CH_4 + 4.09\ O \rightarrow 0.91\ CO + 1.00\ O_2 + 0.95\ H_2 + 1.00\ H_2O + 0.09\ CO_2 + 0.10\ H$$

On the basis of product analyses, a reaction mechanism was proposed. From this reaction mechanism and the reaction stoichiometry the rate of the initial elementary reaction $CH_4 + O \rightarrow CH_3 + OH$ was estimated to be about one-fourth of the overall rate for oxygen atom disappearance, or $\sim 9 \times 10^{13} \exp(-10\,000/RT)$.

Author

INTRODUCTION

Basic information on the reactions of oxygen atoms (O) is of great interest since this knowledge can provide a better understanding of rocket-engine combustion and upper-atmosphere chemistry. Previously, using the mass-spectrometric stirred-reactor tech-

nique described in reference 1, the authors first reported (ref. 2) on the reactions of atomic oxygen with molecular hydrogen, ammonia, and methane in the presence of a large excess of molecular oxygen (O_2). This was followed by a second report (ref. 3) on the $O + H_2$ and $O + NH_3$ reactions with little or no O_2 present. In this second report, detailed kinetic information, such as rate constant, activation energy, and reaction mechanism, was presented. The present investigation deals with the $O + CH_4$ reaction with very little O_2 present. The purpose of reducing the O_2 concentration is to suppress the reactions $H + O_2 + M \rightarrow HO_2 + M$ and $O + O_2 + M \rightarrow O_3 + M$. Although the $O + CH_4$ reaction has been studied before (refs. 4 to 9), many questions still exist. Most of the earlier works (refs. 4 to 6) reported only estimates of the activation energy. Direct measurements of this rate constant based on O-atom decay have been reported only recently (refs. 2 and 9). There are no detailed reaction product analyses for this reaction.

EXPERIMENTAL

Apparatus

The apparatus was essentially the same as that described in reference 2. The 300-cubic-centimeter stirred reactor and its connection to the Bendix time-of-flight mass spectrometer (Model 14-101) is shown in figure 1. The capability of the mass spectrometer for kinetic measurements was improved considerably when the instrument was modified so that it now can monitor six mass peaks simultaneously instead of only two mass peaks. This change was accomplished by replacing the electron-multiplier detector with one containing six channels and adding four more analog output meters.

Oxygen atoms were generated by subjecting a mixture of 1.44 percent O_2 in argon gas to a discharge produced by a 100-watt microwave generator. For our experimental condition the dissociation of O_2 was about 60 percent. Although some excited species, such as O_2 ($^1\Delta_g$), are present with the O atoms, it has been demonstrated by Cadle and Allen (ref. 9) that these excited species do not affect the $O + CH_4$ reaction.

Gases

Methane was commercially available as a tanked gas with a stated 99-percent minimum purity and was used without further purification. This gas was metered using the pressure-drop technique described in reference 2.

The mixture of 1.44 percent O_2 in argon gas was also a commercially available premixed tanked gas. Before using it without further purification it was checked mass spec-

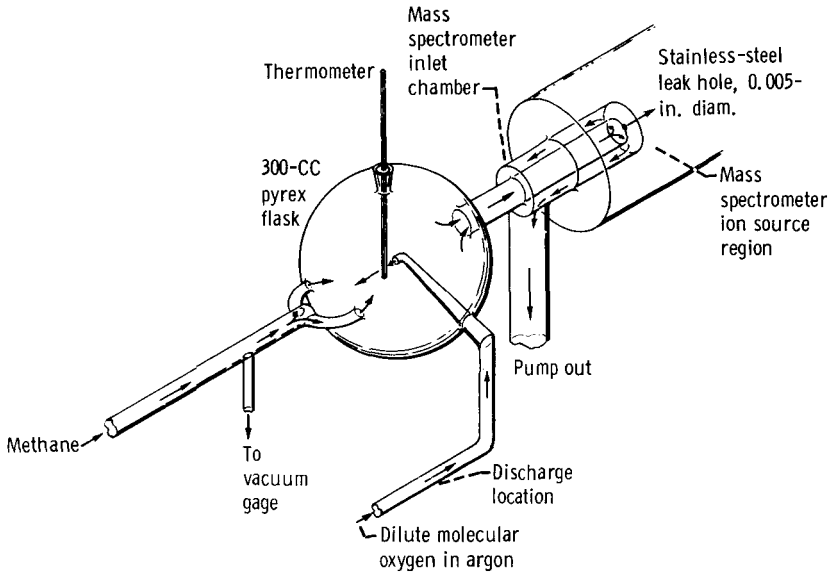

Figure 1. - Stirred reactor and connection to mass spectrometer.

trometrometrically and found to contain only trace impurities. This gas mixture was metered by a small rotameter.

Nitrogen dioxide (NO_2) gas used for the O titration was prepared by adding an excess of O_2 to freshly purified nitric oxide (NO) and used the same day.

Other gases, such as carbon dioxide, carbon monoxide, molecular oxygen, and molecular hydrogen, used to make up calibration gas mixtures for the mass spectrometer with regard to the various reaction products were also tanked gases with a stated purity of at least 99. 5 percent. They were also used without further purification.

Oxygen Atom Monitoring

Oxygen atoms were monitored at a mass-to-charge ratio m/e of 8 with an electron energy of 85 volts because of the interference at m/e = 16 by methane (CH_4) (see ref. 3). The mass spectrometer was calibrated for O by the usual NO_2 gas titration method.

Calculation of Rate Constant

For a simple bimolecular reaction of O with a gas B in a stirred reactor the disappearance of O ($-\Delta[O]$) due to addition of gas B can be expressed as

$$-\frac{\Delta[O]}{\Delta t} = k[O]_f[B]_f \tag{1}$$

where Δt is the residence time of the gas mixture in the stirred reactor, $[O]_f$ is the concentration of O after reaction with gas B, k is the specific rate constant, and $[B]_f$ is the concentration of reactant gas B after reaction with O.

Recombination of O due to the following reactions

$$O + O + M \rightarrow O_2 + M$$

$$O + O_2 + M \rightarrow O_3 + M$$

where M is a third body, is negligible since the O and O_2 concentrations in the present investigation are relatively small.

Precision and Accuracy

Just as in references 2 and 3, the precision of the data was improved by limiting the amount of added methane gas to about 15 percent of the total gas flow. This procedure resulted again in a precision of about ±20 percent, an accuracy of about ±50 percent for the rate constant, and an accuracy of about ±20 percent (~2 kcal) for the activation energy.

The precision of the mass-spectrometer analyses for reaction products was again poor as pointed out in reference 3. Errors due to instrument instability were minimized by measuring all the reaction products simultaneously with the O-atom concentration [O] and expressing these measurements as ratios of [O]. Mass-spectrometer sensitivity to each reaction product was obtained immediately after a run by adding a known amount of the reaction product to the gas flow. The precision for measurements of reaction products as ratios of [O] was again about ±25 percent.

RESULTS

Oxygen Atom Disappearance Due to Addition of Methane

The disappearance of O atoms in the stirred reactor due to the addition of increasing amounts of CH_4 in the presence of low concentrations of O_2 for four different temperatures is shown in figure 2 and given in table I. In figure 2, O-atom disappearance is ex-

TABLE I. - STIRRED REACTOR MEASUREMENTS OF ATOMIC OXYGEN WITH METHANE

[Conditions of normal temperature and pressure.]

Run	Added methane flow, F_{CH_4}, cc/sec	Temperature, T, ^{o}K	Flow into discharge of molecular oxygen in argon gas mixture, $F_{O_2\text{-}Ar}$, cc/sec	Fraction of oxygen atoms consumed in reactor, uncorrected for pressure, $(\Delta[O]/[O]_f)_{unc}$ (a)	Fraction of oxygen atoms consumed in reactor, corrected for pressure, $\Delta[O]/[O]_f$	Pressure, P, mm Hg	Residence time, Δt, sec	Initial oxygen atom flow, F_o, cc/sec	Rate constant for oxygen atom consumption, k^o, cc/(mole)(sec)
1a	0.197	383	1.53	0.28	0.20	0.74	0.14	0.027	4.2×10^8
1b	.623	385	↓	1.08	.87	.82	.12	↓	7.3
2a	.270	386	↓	.58	.47	.75	.13	↓	7.6
3a	.167	389	↓	.29	.22	.73	.14	↓	5.5
3b	.296	389	↓	.61	.49	.76	.13	↓	7.4
3c	.286	389	↓	.79	.67	.76	.13	↓	10.4
4a	.089	390	↓	.26	.22	.72	.14	↓	9.6
4b	.292	↓	↓	.62	.50	.76	.13	↓	7.6
5a	.247	↓	↓	.40	.30	.75	.14	↓	5.2
5b	.491	↓	↓	.95	.78	.80	.13	↓	8.0
							Average value		7.3×10^8
							Average deviation		±17.0 percent
6a	0.081	446	1.53	0.43	0.39	0.71	0.13	0.027	2.5×10^9
6b	.087	446	↓	.61	.57	.72	.13	↓	3.4
6c	.324	447	↓	2.02	1.89	.76	.11	↓	3.5
7a	.062	447	↓	.58	.55	.72	.13	↓	4.5
8a	.066	448	↓	.43	.40	.72	.13	↓	3.2
8b	.170	448	↓	1.12	1.04	.73	.12	↓	3.4
							Average value		3.4×10^9
							Average deviation		±11.0 percent
9a	0.103	487	1.53	1.34	1.29	0.72	0.11	0.027	8.0×10^9
9b	.190	490	↓	2.65	2.57	.74	↓	↓	9.1
10a	.073	495	↓	.94	.90	.72	↓	↓	7.9
10b	.220	496	↓	2.56	2.47	.74	↓	↓	8.0
11a	.089	500	↓	1.21	1.17	.72	↓	↓	8.6
11b	.212	500	↓	3.42	3.33	.74	↓	↓	11.2
							Average value		8.8×10^9
							Average deviation		±10.00 percent
12b	0.033	550	1.53	1.80	1.70	0.71	0.10	0.027	4.5×10^{10}
12c	.039	550	↓	2.14	2.12	.71	↓	↓	4.6
13a	.043	556	↓	2.42	2.40	.72	↓	↓	4.8
13b	.036	557	↓	1.43	1.41	.71	↓	↓	3.4
14a	.108	556	↓	3.63	3.58	.72	↓	↓	2.8
14b	.113	556	↓	7.23	7.18	.72	↓	↓	5.2
14c	.037	558	↓	2.90	2.88	.71	↓	↓	6.6
14d	.037	558	↓	1.55	1.53	.71	↓	↓	3.6
15b	.043	559	↓	2.77	2.74	.72	↓	↓	3.4
							Average value		4.3×10^{10}
							Average deviation		±17.0 percent
				Check runs					
16a	0.059	574	1.45	3.54	3.51	0.70	0.10	0.032	5.1×10^{10}
16b	.077	576	↓	3.70	3.66	.71	↓	↓	4.2
16c	.051	576	↓	2.25	2.22	.70	↓	↓	3.9
16d	.052	576	↓	3.06	3.03	↓	↓	↓	5.2
12a	.056	515	↓	1.32	1.29	↓	.11	↓	1.6
13a	.059	481	↓	.91	.88	↓	.12	↓	8.7×10^9

[a] $\Delta[O] = [O]_o$ (initial oxygen atom concentration) - $[O]_f$ (final oxygen atom concentration).

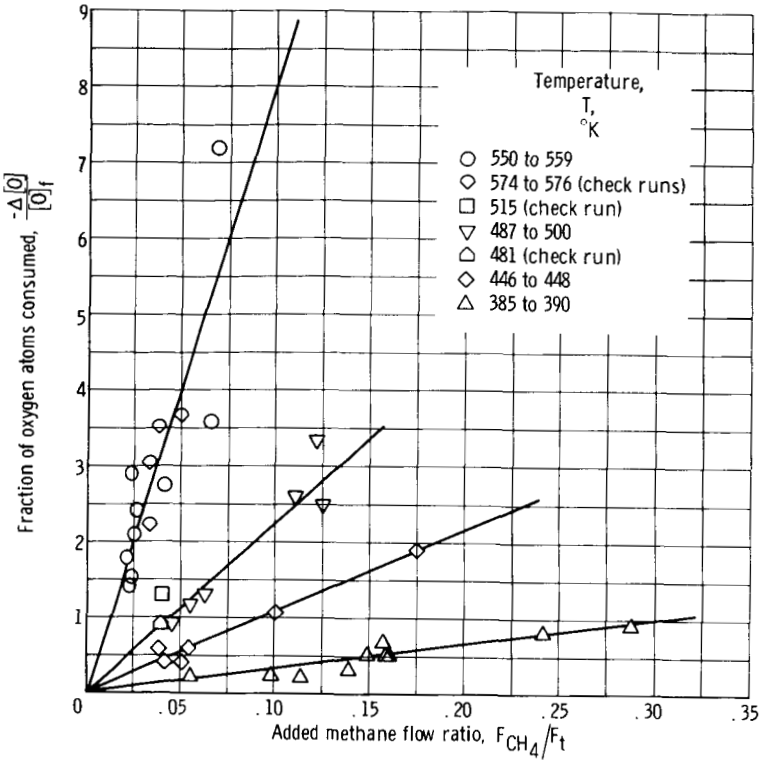

Figure 2. - Oxygen atom disappearance due to reaction with added methane.

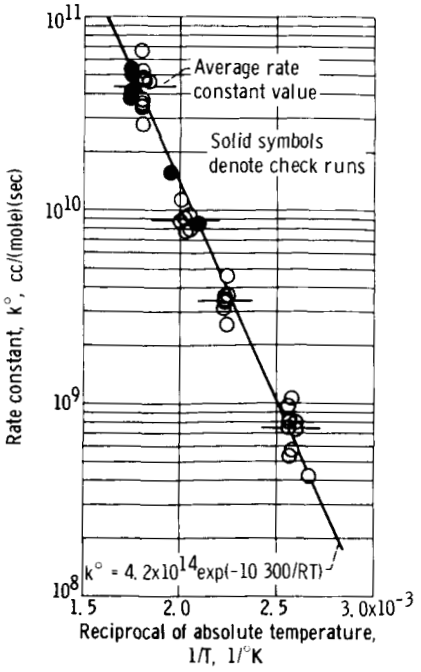

Figure 3. - Rate constants for total oxygen atom disappearance due to reaction with added methane.

pressed as $-\Delta O/[O]_f$, where $-\Delta[O]$ is the initial O concentration $[O]_o$ minus the final O concentration $[O]_f$ after reaction with CH_4 divided by $[O]_f$. Added CH_4 is expressed as F_{CH_4}/F_t, where F_{CH_4} and F_t are methane and total gas flows into the reactor. Equation (1) (recalling that F_{CH_4}/F_t is the mole fraction of methane) shows that a plot of $-\Delta O/[O]_f$ against F_{CH_4}/F_t should be a straight line at constant pressure and residence time Δt in the reactor. Figure 2 shows that straight lines are observed, indicating that the reaction is indeed first order in O and CH_4. This fact has also been observed previously by Cadle and Allen (ref. 9).

Calculation of Overall Rate Constant for Oxygen Atom Disappearance

The overall rate constant for O-atom disappearance k^o due to added CH_4 with low O_2 concentrations was calculated using equation (1). These results are given in table I and shown in figure 3 as an Arrhenius plot of log k^o against $T^{-1}\ {}^oK^{-1}$.

Effect of Molecular Oxygen on Rate of Oxygen Atom Disappearance

The effect of O_2 on the rate of O-atom disappearance can be shown by comparing k^o

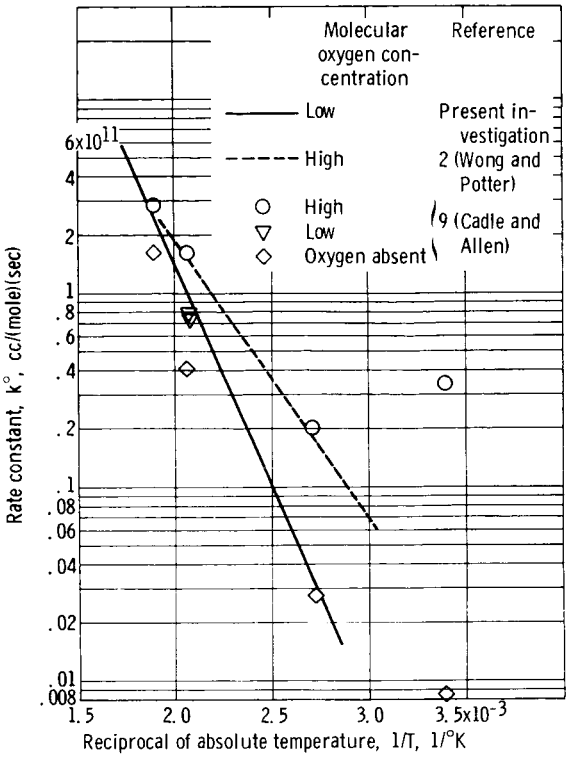

Figure 4. - Effect of molecular oxygen on rate of oxygen atom disappearance for O + CH_4 reaction.

values obtained previously (ref. 2) in the presence of high O_2 concentrations with those obtained in the presence of low O_2 concentrations in the present report. Figure 4 shows a plot of this combined data and demonstrates that an increased rate of O-atom disappearance due to O_2 appears only at the lower temperatures. In addition, in figure 4 the authors' combined data was also compared with the recent O + CH_4 data of reference 9 in which an increase in the rate of O-atom disappearance due to O_2 was also found. The agreement is very good if one considers the fact that the data of Cadle and Allen was obtained by using an entirely different technique: a tube reactor and a photomultiplier technique to monitor [O].

For the case of the O + CH_4 reaction in the presence of high concentrations of O_2 (refs. 2 and 9), Cadle and Allen (ref. 9) have shown that the increased rate of disappearance of O can only be attributed to the influence of ground-state O_2. Molecular oxygen could affect the O + CH_4 reaction by the termolecular reaction $H + O_2 + M \rightarrow HO_2 + M$ followed by subsequent reactions $HO_2 + O \rightarrow O_2 + OH$ and $OH + O \rightarrow O_2 + H$. This reaction sequence increases the rate of O-atom disappearance but does not affect the rate of methane disappearance. This same reaction sequence was used previously in reference 3 to explain the increased rate of O-atom disappearance for the O + H_2 reaction in the presence of a high O_2 concentration.

Reaction Product Analyses

The major reaction products for the O + CH_4 reaction with low O_2 concentrations were carbon monoxide, molecular oxygen, water, and molecular hydrogen. Minor products were carbon dioxide and hydrogen atoms. This finding agreed with the earlier work of Steacie and Parlee (ref. 6) in which no formic acid, formaldehyde, or any other intermediate oxidation product was observed in the O + CH_4 reaction in a tube reactor. The possibility that part of the m/e = 32 peak may be due to methanol CH_3-OH was eliminated by substituting CD_4 for CH_4 and observing that the m/e = 32 peak did not shift and that the m/e = 36 peak did not increase during the reaction of O + CD_4.

TABLE II. - REACTION PRODUCT RATIO MEASUREMENTS

Temperature, T, °K	Reaction-product ratio				
	$\Delta[O]/\Delta[O_2]$	$\Delta[O]/\Delta[CO]$	$\Delta[O]/\Delta[H_2]$	$\Delta[O]/\Delta[CO_2]$	$\Delta[O]/\Delta[H_2O]$
397	3.8	---	3.4	--	--
443	3.3	---	---	--	--
455	6.4	---	---	51	--
456	---	---	---	--	(a)
460	3.1	4.9	---	69	--
557	3.5	---	4.4	--	--
560	3.3	5.7	---	--	(a)
561	5.0	2.9	---	37	--
Average	4.1	4.5	3.9	52	~4

[a]Approximates the value for $\Delta[O]/\Delta[O_2]$.

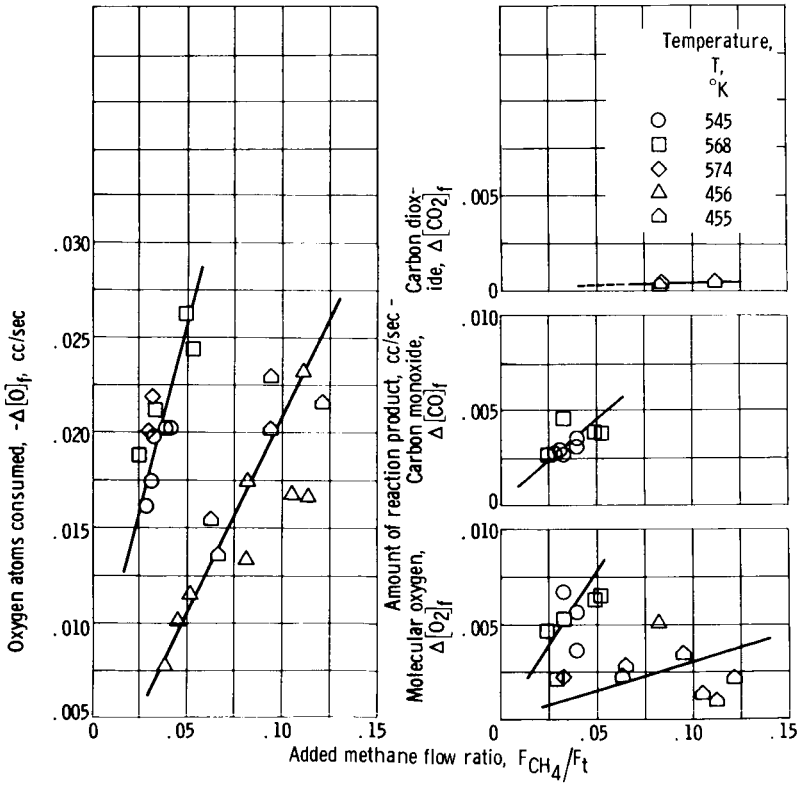

Figure 5. - Oxygen atom decay and reaction product measurements at conditions of normal temperature and pressure.

Typical O-atom disappearance and reaction product measurements are shown in figure 5. Figure 5 shows the O-atom disappearance $-\Delta[O]_f$ and some of the resulting reaction products $-\Delta[\text{reaction product}]_f$. Just as in reference 3, no attempt was made to calibrate the mass spectrometer for small amounts of water because of the difficulties involved. The measurements of the water concentration $\Delta[H_2O]$ were in terms of ion current only, relative to the oxygen concentration $\Delta[O_2]$. The amount of atomic hydrogen $\Delta[H]$ was also estimated on the basis of its ion current value, relative to the carbon dioxide concentration $\Delta[CO_2]$.

From such data as figure 5, one can obtain ratios of $-\Delta[O]_f$ to $\Delta[\text{reaction products}]$. Just as in reference 3 these ratios were obtained by drawing mean lines through the data and dividing the slope of the $-\Delta[O]_f$ line by the slope of $\Delta[\text{reaction product}]$ line. The results of these ratio measurements are summarized in table II.

Reaction Stoichiometry

With the preceding information the reaction stoichiometry can now be obtained as shown in reference 3. By assigning arbitrary values of x and y to the moles of molecular hydrogen and molecular oxygen produced in this reaction, by knowing that the only carbon containing products were carbon monoxide and carbon dioxide in the ratio of 10 moles of carbon monoxide to 1 mole of carbon dioxide and by estimating that molecular and atomic hydrogen were also in the same ratio, the $O + CH_4$ reaction can be written as

$$CH_4 + (2y + 3.09 - 1.05\,x)O \rightarrow yO_2 + 0.91\,CO + xH_2 + 0.1\,xH + (2 - 1.05\,x)H_2O + 0.09\,CO_2 \quad (2)$$

With only two unknowns, the complete stoichiometry can be obtained from two ratio measurements. If the two most reliable ratio measurements $\Delta[O]/\Delta[O_2]$ and $\Delta[O]/\Delta[CO]$ are used, the following equations can be set up and solved for x and y:

$$\left.\begin{aligned} \frac{\Delta[O]}{\Delta[O_2]} &= \frac{2y + 3.09 - 1.05\,x}{y} = 4.1 \\ \frac{\Delta[O]}{\Delta[CO]} &= \frac{2y + 3.09 - 1.05\,x}{0.91} = 4.5 \end{aligned}\right\} \text{independent of temperature}$$

It was found that $x = 0.95$ and $y = 1.00$; thus equation (2) becomes

$$CH_4 + 4.09\,O \rightarrow 1.00\,O_2 + 0.91\,CO + 0.95\,H_2 + 0.10\,H + 1.00\,H_2O + 0.09\,CO_2 \quad (3)$$

From equation (3), $\Delta[O]/\Delta[H_2] = 4.3$, which agrees well with the experimental value of 3.9 (table II, p. 8), and $\Delta[O]/\Delta[H_2O] = 4.1$, which also agrees with the experimental value of ~4 (table II).

Further support for the validity of equation (3) was obtained by measuring $\Delta[O]/\Delta[CH_4]$. Earlier attempts to measure $\Delta[O]/\Delta[CH_4]$ by using the 300-cubic-centimeter reactor were unsuccessful since the amount of CH_4 consumed in the reaction $-\Delta[CH_4]$ was too small to be measured reliably (refs. 3 and 9). A second attempt to measure $\Delta[O]/\Delta[CH_4]$ was made by using a 2-liter reactor. The results are given in table III.

TABLE III. - MEASUREMENT OF METHANE REACTION PRODUCT RATIO

[Conditions of normal temperature and pressure.]

Run	Oxygen consumed, $-\Delta[O]$, cc/sec	Initial added methane, $[CH_4]$, cc/sec	Fraction of methane consumed measured mass spectrometrically, $\left(-\Delta[CH_4]/[CH_4]_o\right)_{ms}$	Methane consumed, $-\Delta[CH_4]$, cc/sec	Reaction product ratio, $\Delta[O]/\Delta[CH_4]$
1	0.025	0.0400	0.13	0.0052	4.8
2	.012	.0115	.26	.0030	4.0
3	.013	.0092	.26	.0024	5.4
					av 4.7

The average of 4.7 for the three measurements agreed well with our calculated reaction stoichiometry value of 4.1. It is interesting to note that in our previous work (ref. 2) the reaction stoichiometry for this reaction in the presence of a high concentration of O_2 was reported to be about 8.

DISCUSSION

Proposed Reaction Mechanism

On the basis of the reaction product analyses, a possible reaction mechanism for the $O + CH_4$ reaction when the O_2 concentration is low enough to neglect the reactions $O + O_2 + M \rightarrow O_3 + M$ and $H + O_2 + M \rightarrow HO_2 + M$ could consist of the following reactions:

$$O + CH_4 \rightarrow CH_3 + OH \tag{4}$$

$$CH_3 + O \rightarrow CH_2 + OH \tag{5}$$

$$CH_2 + O \rightarrow CO + 2H \tag{6}$$

$$OH + O \rightarrow O_2 + H \tag{7}$$

$$H + CH_4 \rightarrow CH_3 + H_2 \tag{8}$$

$$CO + OH \rightarrow CO_2 + H \tag{9}$$

$$CH_4 + OH \rightarrow H_2O + CH_3 \tag{10}$$

Reaction (4) is the initial propagation step involving a hydrogen atom abstraction process to produce methyl (CH_3) and hydroxyl (OH) radicals. Reactions (5) and (6) are expected to be very fast successive reactions of CH_3 and CH_2 with O. Reaction (7) is known to be fast (ref. 10) and is used to account for O_2. Reactions (8) and (10) are selected because of the presence of excess CH_4 to account for molecular hydrogen and water reaction products. Reaction (9) is used to account for carbon dioxide since the O + CO reaction is so slow.

Calculation of Rate Constant for $CH_4 + O \rightarrow CH_3 + OH$ Reaction

If the reaction mechanism involving reactions (4) to (10) is used, the same technique that was used in reference 3 can be used to obtain a value for k_4, the rate constant for the initial elementary step $CH_4 + O \rightarrow CH_3 + OH$. Assuming a steady state for CH_2, one can show that

$$k_4 = \frac{\Delta[O] - 2\left(\Delta[CO] + \Delta[CO_2]\right) - \Delta[O_2]}{\Delta t[O][CH_4]} \tag{11}$$

where the differentials have been replaced by finite differences appropriate to the stirred reactor. In equation (11) the terms $\Delta[CO]$, $\Delta[CO_2]$, and $\Delta[O_2]$ can be replaced by $\Delta[O]$ based on the experimental reaction product ratios. The rate constant k_4 is now equal to

$$\frac{\Delta[O](1 - 0.72)}{\Delta t[O][CH_4]} = \frac{0.28\,\Delta[O]}{\Delta t[O][CH_4]} \tag{12}$$

and since k^O, total consumption, is equal to $-\Delta[O]/\Delta t[O][CH_4]$, k_4 can be related to k^O:

$$k_4 = 0.27\, k^O$$

$$= \frac{1}{3.7} \frac{\Delta[O]}{\Delta t[O][CH_4]} \qquad (13)$$

On the basis of the reaction stoichiometry, k_4 can also be related directly to k^O. Since $\Delta[O]/\Delta[CH_4] = 4.1$ and $k_4 = (1/4.1)\, k^O$, this relation is in fair agreement with equation (13). Thus, the set of proposed reactions (4) to (10) is consistent with the experimental facts.

With the relation shown in equation (13), k_4 values were calculated and plotted in figure 6. The k_4 line $8.6 \times 10^{13} \exp(-10\,000/RT)$ is compared with the k_4 value deduced by Azatian, et al. (ref. 8) on the basis of their flame ignition work. There is fair agreement between the two sets of data.

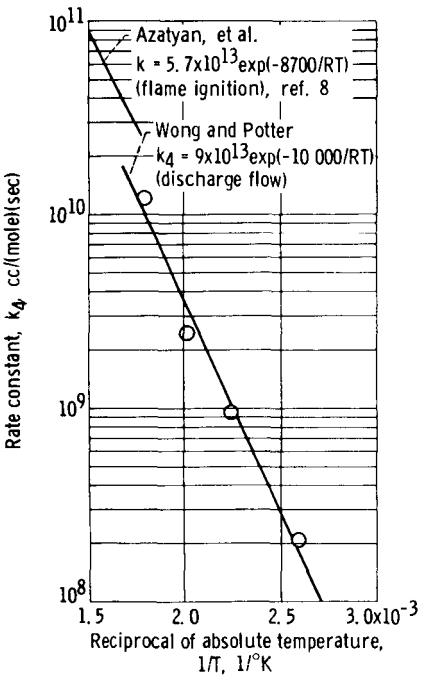

Figure 6. - Rate constants for $CH_4 + O \rightarrow CH_3 + OH$ reaction.

Comparison of Activation Energy for $O + CH_4$ Reaction

It was found that for low O_2 concentrations the activation energy ΔE of the $O + CH_4$ reaction is ~10 kilocalories per mole, while for high O_2 concentrations $\Delta E \approx 7$ kilocalories per mole (ref. 2) (see fig. 4, p. 7). This lowered ΔE is believed to be the result of the reaction sequence $H + O_2 + M \rightarrow HO_2 + M$, $HO_2 + O \rightarrow OH + O_2$, and $OH + O \rightarrow O_2 + H$. Figure 4 shows that the effect of this reaction sequence on O-atom disappearance decreases with increasing temperature. This is due to the fact that at high temperatures the rate of the bimolecular oxidation becomes much faster than the rate of the termolecular $H + O_2 + M \rightarrow HO_2 + M$ reaction. In support of the present findings are the works of Steacie and Parlee (ref. 6) and Cadle and Allen (ref. 9). Steacie and Parlee (ref. 6) reported ΔE to be ~8 kilocalories per mole at 303° K and ~11 to 13 kilocalories per mole at 473° to 603° K. Cadle and Allen (ref. 9) reported that this effect of O_2 on the rate of O-atom disappearance decreases at higher temperature.

CONCLUSIONS

A mass-spectrometric technique was used to study the reaction $CH_4 + O$ in the presence of low molecular oxygen concentrations for the temperature range 375° to 576° K. This investigation resulted in the following conclusions:

1. Rate constants for total oxygen atom disappearance in the $O + CH_4$ reaction were measured and found to be in good agreement with those obtained by other investigators.

2. The presence of high molecular oxygen concentrations resulted in an increase in the rate of oxygen atom disappearance. This increase was attributed to the reaction of ground-state molecular oxygen with hydrogen atoms in the reaction sequence $H + O_2 + M \rightarrow HO_2 + M$, $HO_2 + O \rightarrow OH + O_2$, and $OH + O \rightarrow O_2 + H$.

3. The following reaction stoichiometry was obtained based on reaction product analyses: $CH_4 + 4.09\ O \rightarrow 1.00\ O_2 + 0.91\ CO + 0.95\ H_2 + 0.10\ H + 1.00\ H_2O + 0.09\ CO$.

4. A reaction mechanism was proposed for the methane-atomic oxygen reaction based on the reaction product analyses.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 18, 1966.

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